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(54) RECOVERY OF ACIDS FROM AQUEOUS SOLUTIONS

(71) We, IMI (TAMI) INSTITUTE FOR RESEARCH & DEVELOPMENT, an Israeli Company, of Haifa Bay, Near Ir Ganin, Haifa, Israel, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:

THIS INVENTION concerns the recovery of acids from aqueous solutions.

The recovery of acids from aqueous solutions is necessary in various technical fields. Thus, for example, certain organic acids which are the fermentation products produced by various microorganisms in aqueous nutrient media have to be recovered in as pure and concentrated a state as possible from the fermentation broth. This applies, for example, to citric acid, lactic acid and certain antibiotics such as penicillin. In other cases, it would be desirable to recover acids from industrial effluents where such recovery presents an economic advantage.

A number of methods for recovering acids from aqueous liquors are known, for example:

(a) Precipitation of the acid in the form of a sparingly soluble salt, and subsequent decomposition of salt into the acid.

(b) Extraction with an organic solvent which is partly or wholly immiscible with water, such as certain aliphatic alcohols, ketones and ethers.

(c) Extraction with a water-insoluble amine, generally in the form of a solution of the amine in a substantially water-immiscible organic solvent, followed by the decomposition of the amine salt thus formed with an acid or a base;

(d) Extraction with an amine salt. This is a variant of the extraction outlined in paragraph (c). In some cases the amount of acid that can be extracted with the aid of a water-immiscible amine is

stoichiometrically considerably in excess of the amine present in the amine solution. The possible excess amount of extracted acid depends on several parameters, e.g. the concentration of the acid in the aqueous solution from which the acid is to be extracted and the nature of the amine and of its solvent. In several cases this phenomenon has been used to extract acids from concentrated aqueous solutions thereof using as extractant, a salt derived from an amine and the acid to be extracted. From the extract the excess of acid can be recovered by washing with water or, in the case of volatile acids, by distillation.

Precipitation of salts is a straightforward method but is not a suitable method in many cases.

Extraction with an organic solvent is used, for example, to recover phosphoric acid from the sludges produced by the acidulation of rock phosphate with sulphuric or hydrochloric acid, and for the purification of crude phosphoric acid. It is useful in many cases, but it presupposes that the concentration of the acid to be extracted in the aqueous system from which it is to be extracted is relatively high.

An advantage of the method in which amines are used as extractants is that in such a method a favourable coefficient of distribution of the acid to be extracted between the aqueous and amine phases used in the extracting process is obtained, and as a result the acid can be extracted even from highly dilute solutions. This method does have its disadvantages, however, for example, the need to decompose the recovered amine salt in order to regenerate the desired acid and to separate and recover the amine extractant, which it is desirable to recycle since amines are much too expensive to be thrown away, often presents problems. As a rule, the amine

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extractant is liberated by treatment of the amine salt with an inorganic base, e.g. calcium hydroxide, and this produces a salt of the desired acid instead of the free acid itself. In addition to the expenditure of chemicals, this process has the disadvantage of requiring a number of processing steps. In the case of lower amines, it has also been suggested to liberate the amine from the amine salt by steam distillation whereby the salt is decomposed and the amine is simultaneously distilled off. This method is not applicable to amines of higher molecular weight, which are the amines which are generally preferred for extracting the acid from the aqueous system.

A method of extracting sulphuric acid from an aqueous solution thereof which also contains ions of common metals, in particular iron, has been suggested. This method requires the use of an extractant which comprises a tertiary amine of specific structure in which the nitrogen atom is connected to three methylene groups bearing alkyl radicals having branching on the carbon atom nearest the nitrogen atom, and/or aryl radicals, to produce a solvent extract containing the amine sulphate which sulphate can be decomposed into the desired sulphuric acid by treatment of the extract with water. Recovery of the aqueous phase yields the liberated sulphuric acid. Other amines not of the structure specified (such as tri-iso-octyl amine) cannot be used in this method.

The extraction with amine salts also requires that the concentration of the acid to be extracted in the aqueous system from which it is to be extracted is relatively high. Consequently this method has been suggested particularly for purposes such as the recovery of volatile acids from relatively concentrated aqueous solutions thereof.

The present invention provides a process for the extraction of an acid from an aqueous system using, as extractant, a solution of at least one high molecular-weight amine in an organic solvent, in which the extraction of the acid takes place with a high degree of selectivity even from highly dilute systems, the acid can readily be recovered from the solution of the resultant amine salt in the organic solvent, and if desired, after regeneration of the desired acid from the said amine salt, the resultant solution of the amine in the organic solvent can be recycled for the extraction of more acid from the aqueous system.

According to the present invention there is provided a process for the recovery of an acid from an aqueous solution, which comprises extracting the aqueous solution

of the acid with a water-immiscible organic extractant comprising at least one secondary or tertiary amine in which the total number of carbon atoms per molecule is at least 20, dissolved in a water-immiscible organic non-polar or polar solvent, separating the organic extract from the residual aqueous phase and, stripping at a temperature higher than the temperature at which the extraction is performed, the organic extract with water to obtain an aqueous phase containing a substantial part of the acid and an organic phase containing substantially all the amine; and separating the aqueous back-extract from the organic phase.

For the sake of brevity the term "extractant" will be used throughout this specification to denote the solution of amine in the water-immiscible organic polar or non-polar solvent, the term "extract" will be used to denote the organic phase comprising the extractant and the acid extracted by the extractant from the original aqueous solution of the acid and the term "back-extract" will be used to denote the aqueous solution of the acid produced by stripping (back-extracting) the acid from the extract.

Examples of amines which are suitable for use in the present process are aliphatic, araliphatic or aromatic amines, or mixed aliphatic-araliphatic or aliphatic-aromatic amines, or mixtures of such amines, the amines having a total of at least 20 carbon atoms.

Where mixtures of two or more amines are used, e.g. commercial trialkylamines which usually contain some secondary alkylamines, it is sufficient, for the purposes of this invention, if the average total number of carbon atoms is at least 20 for each nitrogen atom of the amines.

Amines having a total of less than 20 carbon atoms per molecule are not suitable for use in the process according to the invention, being less suitable the smaller the total number of carbon atoms, because such amines and their salts with the acids to be extracted are insufficiently soluble in the organic phase and much too soluble in the aqueous phase and they tend to dissolve in the aqueous acid solution from which the acid is to be extracted. Moreover, the amine salts of the extracted acid tend to crystallize out of the extract.

Certain commercial tertiary straight-chain or branched-chain alkylamines in which each alkyl group has from 8 to 13 carbon atoms, or mixtures thereof with secondary amines containing similar alkyl groups, have been found to be particularly satisfactory for use as components of the extractant of the present process, e.g. tri-n-caprylamine, tri-n-laurylamine and tri-

tridecylamine (with branched alkyl groups). Secondary amines in which one of the hydrocarbyl groups has at least 12 carbon atoms and the other at least 8 carbon atoms, e.g. those sold commercially under the name "Amberlite LA-1" have also been found suitable. ("Amberlite" is a registered Trade-Mark).

In the process according to the invention, various water-immiscible organic solvents, both non-polar and polar, can be used as a component of the extractant, for example, aliphatic and aromatic hydrocarbons, petroleum fractions, hydrocarbons substituted with nitro groups or halogen atoms and alcohols, or mixtures thereof.

The process according to the invention can advantageously be performed as a continuous process. In this case the organic solvent from which the acid has been recovered by stripping (back-extraction) is recycled for use as a component in the extractant and, before or while being thus recycled, is cooled, or allowed to cool, to the temperature at which the extraction is being performed. Alternatively, especially when operating on a small scale, the process may be carried out as a batch process in which a batch of the aqueous acid solution is subjected to one or a number of extracting operations. In the latter case, if the organic solvent from which the extracted acid has been recovered is recycled for a second, third or even fourth extracting operation, it need not necessarily be cooled before being contacted again with the aqueous solution to be extracted, since a gradual rise of the temperature at which the extraction takes place can be tolerated in this case.

It is to be understood that the terms "lower temperature" and "higher temperature" are not used in absolute terms. The important feature of this invention is the difference in the temperature of the extraction and stripping. This is usually at least 20°C, both for operational convenience and in order to make both the extraction and the stripping as complete as possible. The extraction may be carried out at temperatures as low as near the freezing point of the aqueous acid solution, and the temperature of the stripping may be at or near the boiling point of the extract or the aqueous back-extractant at atmospheric pressure, or if the stripping is carried out under elevated pressure, at an even higher temperature, e.g. a temperature above 100°C, always on condition that the temperature and pressure are so chosen that the amine remains in the organic phase. In many cases the extraction can be carried out at or near room temperature, and the stripping at a temperature of 20 to 40°C

above room temperature. Usually, the extraction is performed at room temperature and the stripping is performed at 80°C or higher. As a rule, the stripping is more effective the higher the stripping temperature, but the extraction and stripping temperatures will be selected in individual cases in accordance with practical factors such as corrosion resistance and the cost of the equipment, cost of heating and cooling of the streams of the acid solution, the extract and the extractant, and the required concentration of recovered acid.

Since water is used for stripping, the back-extract is an aqueous solution of the free acid. However, if it is desired to obtain a part of the acid in the form of an aqueous solution or a salt thereof, it is possible to adjust the extent of the back-extraction with water so as to leave a part of the acid in the solvent phase. This remaining part of the acid can then be stripped with an aqueous alkali metal hydroxide or alkali metal salt solution (in this context "alkali metal" includes ammonium) to yield the corresponding alkali metal salt of the extracted acid. Alternatively, an aqueous alkali metal (including ammonium) chloride, for example, can be used for the back extraction. In this case, too, the back-extract contains the corresponding alkali metal salt of the extracted acid while the amine in the extractant is converted into its hydrochloride which must then be decomposed, e.g. by treatment with calcium hydroxide, for re-constituting the extractant.

The best temperature for the extraction and stripping and the most suitable composition of the extractant as regards both the amine and the solvent will depend on a number of factors, e.g. the kind of acid to be extracted, its concentration in the original aqueous solution, and the impurities present in the solution. The major aim in both the extraction and stripping will be to achieve as favourable a distribution coefficient as possible for the distribution of the acid between the aqueous and organic phases. In the extraction, this has to be in favour of the extractant, in the stripping, in favour of the aqueous phase.

Before the extract is subjected to stripping it may in some cases be desirable to change its composition in order to render the stripping more efficient. Thus, it may be desirable to remove some of the solvent, e.g. by distillation *in vacuo*; to add some solvent, which can be the same as, or different from, the solvent used in the extractant, or to remove at least some of the extractant solvent and to replace it with a different solvent; or to add other auxiliary substances that may serve to facilitate the

back-extraction of the desired acid into the aqueous phase.

After the stripping the residual organic phase may be subjected to such operations as may be required or desired for purifying it or changing or reconstituting its composition, e.g. by the removal of retained impurities or by-product acids which have been co-extracted with the main acid but have not been back-extracted into the aqueous back-extract, by the removal of a second solvent or of auxiliary substances that may have been added to the extract before the stripping operation, by the addition of make-up solvent and/or amine or by cooling, and then if desired, recycled for use as extractant.

The present invention is particularly useful for the recovery of citric acid from fermentation broths containing it. These broths contain large amounts of organic and some inorganic impurities. Oxalic acid is one such contaminant of citric acid broths and can be co-extracted into the extractant when citric acid broths are extracted using the present process. However, the oxalic acid remains in the extractant during the stripping thereof and can be recovered by contacting the stripped extractant with water under pressure at a temperature from 120° to 160°C.

Present techniques for the recovery and purification of citric acid have not proceeded beyond the classical steps of precipitating calcium citrate from the broth by the addition of calcium hydroxide, separating the calcium citrate, decomposing it with sulphuric acid, removing the aqueous solution of citric acid from the precipitated calcium sulphate and afterwards evaporating the water and purifying the still rather impure citric acid by a number of successive operations such as selective precipitation, ion exchange and treatment with active carbon. This entire process is expensive because of the relatively large number of operations which it requires and the expenditure of chemicals and energy, and is wasteful owing to low yields. The situation is not much better with other fermentation processes, e.g. in the manufacture of lactic acid. Suggestions to the effect that organic acids may be recovered from aqueous solutions thereof, in particular from fermentation broths, with the aid of long-chain aliphatic amines have been made in the literature but have apparently not yet found industrial application.

In general it is found that no, or almost no water dissolves in the extractant, and *vice versa*. It is also found that the concentration of the extracted acid in the back-extract is usually at least as concentrated as it is in the original aqueous

solution from which it has been extracted, and in many cases even more concentrated. The process according to the invention can thus be used in order both to purify and to concentrate the acid. In the case of citric acid, the back-extract is so pure that food-grade citric acid can directly be recovered from it.

The extraction is usually performed as a multi-stage continuous counter-current process and the extractant having had the desired acid removed from it by back-extraction, is cooled or is allowed to cool to the temperature at which the extraction is performed and is continuously recycled to the extraction.

The invention will now be illustrated further by the following Examples.

Example 1

Crude broth from the citric acid fermentation of sucrose was extracted at ambient temperature in three separatory funnels in simulation of a three-stage counter-current extraction system, each funnel being supplied in turn with portions of 100 g of the broth and 148 g of an extractant composed of 50% w/w of tri-tridecylamine and 50% w/w of xylene. Samples of the extracts and raffines from the three-stage system were analysed until two successive samples showed substantially identical analysis which indicated that steady state had been reached. The operation was continued, combining the steady-state extracts containing 10% by weight of citric acid, until enough extract had been collected to permit a similar stripping of the extract to be performed in analogous manner. The stripping was performed at 80°C, also in a 3-stage separatory funnel system, using 1 part by weight of water for every 2.5 parts of extract as extractant. At steady state, every 100 g of the original crude broth yielded 80 g of a pure aqueous back-extract containing 20% w/w of citric acid.

Example 2

100 g of the crude citric acid broth of Example 1 were extracted at 25°C in two counter-current stages (simulated by two separatory funnels) with 120 g of an extractant containing 50% w/w of tri-laurylamine and 50% w/w of xylene to yield 136g of an extract containing 12% w/w of citric acid. The extract was diluted with a further 60 g of xylene and then stripped at 80°C in three simulated counter-current stage with 38 g of H₂O to yield 55 g of a back-extract containing about 16 g of pure citric acid, i.e. a purified aqueous solution containing 29% w/w of citric acid as compared to 16.4% in the crude feed. After the back-extraction the organic extractant phase weighed 180 g; it consisted essentially of 33% w/w of tri-laurylamine and 67% w/w of xylene and was practically

free from citric acid. 60 g of xylene were removed therefrom by distillation. The distillation residue of 120 g was reconstituted extractant which was ready for recycling.

5 Example 3

Extraction of crude citric acid broth was carried out as described in Example 2 to give 136 g of an extract containing 12% w/w of citric acid, which was stripped by heating with 80 g of H₂O to 140°C, in an adapted Carius pressure vessel. A sample, taken under pressure through a tube dipping into the aqueous back-extract phase, showed that the aqueous phase contained 14% w/w of citric acid, corresponding to a total amount of citric acid in the back-extract of 13 g.

This Example shows that if the back-extraction is effected at an elevated temperature under pressure, it is not necessary to dilute the extract before the back-extraction. Accordingly no diluent has to be removed from the extractant before it is recycled.

25 Example 4

100 g of a 12.8% w/w crude citric-acid broth were extracted at 25°C in four counter-current stages with 145 g of extractant containing 25% w/w of technical-grade trioctylamine and 75% w/w of a petroleum fraction boiling at 140° — 210°C. A three-phase system, viz. an aqueous phase and two organic extract phases, was formed. At the 4th stage the upper extract phase (about 93 g) contained 0.2% w/w of citric acid and about 5.6% w/w of amine and the lower extract phase (about 65 g) contained about 19.5% w/w of citric acid and about 48% of amine. The two extract phases were handled together and were stripped at 100°C in a single stage with 60 g of H₂O to yield about 73 g of a back-extract containing about 12.7 g of citric acid i.e. a concentration of 17.5% w/w of citric acid. At the same time 145 g of an homogeneous organic extractant phase was obtained, which was ready to be recycled after cooling.

Example 5

100 g of an 18% w/w crude citric acid broth were extracted at 40°C in five counter-current stages (simulated by five separatory funnels) with 220 g of recycled extractant containing 34% w/w of triauryl amine, 5% w/w of dilauryl amine, 53% w/w of a petroleum fraction boiling at 180-210°C, 5% w/w of 1-n-octanol and 3% w/w of citric acid. The aforesaid mixture of triaurylamine and dilaurylamine is a commercial product. The extract amounted to 237 g and contained 10% w/w of citric acid. It was stripped at 65°C in five simulated counter-current stages with 96 g of H₂O to yield 113 g of an aqueous back-extract containing 15% w/w of pure

citric acid. At the same time 220 g of extractant phase was obtained which was ready to be recycled after cooling.

The presence of the 1-n-octanol in the extractant prevented the stratification of the extract described in Example 4.

Example 6

200 g of a 10% w/w crude citric acid broth were extracted at 25°C in three counter-current stages (simulated by three separatory funnels) with 230 g of an extractant containing 36% w/w of triaurylamine, 57% w/w of a petroleum fraction boiling at 180-210°C, and 5% w/w of octanol. The extract amounted to 250 g and contained 8% w/w of citric acid.

One-half of the extract (125 g) was back-extracted at 40°C in four simulated counter-current stages with 90 g of H₂O to yield 96 g of a back-extract containing 6 g of pure citric acid i.e. a purified aqueous solution containing 6% w/w of citric acid, which amounted to a 60 percent recovery.

The other half of the extract (125 g) was similarly back-extracted but at 60°C, and yielded 100 g of a back-extract containing about 10 g of pure citric acid; i.e. a purified aqueous solution containing about 10% w/w of citric acid, which was a substantially 100 percent recovery.

This Example shows that the stripping is more efficient if a temperature difference between the extraction and stripping of 35°C is used rather than a temperature difference of only 15°C.

Example 7

100 g of a 10% w/w crude citric acid broth was contacted in a separatory funnel at room temperature with 100 g of an extractant containing 50% w/w of tri-tridecylamine and 50% w/w of nitrobenzene. After shaking and phase separation it was found that over 90% of the citric acid had transferred to the extract which thus contained 9.3% w/w of citric acid. This extract was treated in two steps.

First 100 g water was added to the extract at 60°C and stripped. At this stage the back-extract contained only 13% of the initial citric acid i.e. the back-extract contained 1.3% w/w of citric acid. 150 g of low-boiling hydrocarbon fraction with a boiling temperature of 60-90°C was then added to the separating funnel still containing both phases, and further extraction gave a back-extract with a citric acid concentration of 7.5% w/w. Thus the amount of back-extracted citric acid was 7.5 g which corresponds to a 75% recovery in a single contact.

This Example shows that although nitrobenzene is a good extractant solvent, the result extract can not readily be back-extracted unless a hydrocarbon fraction is added to it.

Example 8

Extraction of crude citric-acid broth was carried out as described in Example 2. The extract, weighing 136 g and containing 12% w/w of citric acid, was stripped at 80°C in a single stage with 12.5 g of H₂O. The aqueous back-extract weighed 17 g and contained 4.5 g of pure citric acid. The residual citric acid remaining in the extract (which at this stage weighed 131.5 g) was then back-extracted with 18.5 g of a 40% w/w aqueous NaOH solution. All the residual citric acid was thus converted into trisodium citrate. This salt was recovered from its aqueous solution in a highly pure state (yield 16 g).

Example 9

Extraction of crude citric-acid broth and single-stage stripping of the extract were carried out as described in Example 8. The residual citric acid remaining in the organic phase (the said phase weighed 131.5 g) was back-extracted in two counter-current stages with 14 g of a 26% w/w aqueous NaCl solution, whereby the residual citric acid converted into monosodium citrate and passed into the aqueous phase; the amine in the organic phase was converted into its hydrochloride. The phases were separated and the organic phase was treated with an aqueous slurry of Ca(OH)₂ whereby the free amine was regenerated. The calcium chloride solution was discarded as waste.

Example 10

A bench-scale unit was set up comprising an extraction section of four mixer-settler units, and a stripping section of four mixer-settler units. The mixer-settler units corresponded to those described in the US Patent No. 3,489,526, of appropriate size. The four units of the stripping section were provided with hot-water coils to permit operation at temperature around 80°C.

The extraction section was fed with 1000 g/hr (900 ml/hr) of crude citric acid broth containing 15.7% w/w of citric acid, and counter-current thereto 1500 g/hr (1800 ml/hr) of an extractant composed of a 40% w/w solution of technical-grade triauryllamine in a petroleum fraction (boiling range 140°-210°C) containing 3-5% by weight of *n*-octanol. When steady state was attained, the extract 1655 g/hr (1800 ml/hr) containing 9.9% w/w of citric acid, was fed through a preheater to the stripping section where the temperature was maintained at 80°C, and hot water was then added thereto at a rate of 360 ml/hr counter-current to the extract to strip the citric acid therefrom. When steady state was attained the back-extract contained 28% w/w of pure citric acid. The stripped extractant was cooled and recycled to the extraction section. The

aqueous back-extract was evaporated to give pure crystalline citric acid.

Example 11

100 g of the aqueous wash liquor obtained by washing a crude citric acid filter cake and containing 5% w/w of citric acid was extracted with 30 g of a 1:1 w/w mixture of Amberlite LA-1 (trade name of a liquid secondary amine containing 23-26 C atoms) and the petroleum fractions used in Example 4. The extraction was effected at room temperature in three stages in a separatory-funnel simulation of a counter-current extraction. The extract was contacted in four stages with 25 ml of water at 90°C, whereby an aqueous back-extract containing 15% w/w of citric acid was obtained.

Example 12

100 g of a crude dilute aqueous lactic acid liquor containing 2% w/w of lactic acid was contacted in three counter-current stages with 40 g of an extractant composed of 50% w/w of tri-tridecylamine and 50% w/w of *n*-octanol. The extract was stripped with 40 g of water at a temperature near its boiling point in five counter-current stages. About 2 g of free lactic acid was obtained as a 5% w/w aqueous solution.

Example 13

100 g of a 10% w/w aqueous lactic acid solution was extracted in a separatory funnel simulation of a two-stage counter-current extraction system with 130 g of an extractant consisting of 50% w/w of trioctylamine and 50% w/w of a petroleum fraction boiling at 140°-210°C. The extract, containing 7.5% of lactic acid, was stripped with 54 g of water in a similar three-stage counter-current system at 80°C. The aqueous back-extract amounted to about 63 g and contained about 9.5 g of pure lactic acid.

Example 14

100 g of an 8% w/w aqueous H₃PO₄ solution was extracted with a mixture of triauryllamine (40% w/w) and a petroleum fraction boiling at 140°-210°C (60% w/w) in a three-stage counter-current system at 25°C. 130 g of extract, containing 6% w/w of H₃PO₄, was obtained. The extract was stripped with 20 g of water at 80°C in three counter-current stages. The back-extract consisted of about 28 g of 25% w/w of pure aqueous H₃PO₄.

Example 15

Crude citric-acid broth from the citric acid fermentation of sucrose may contain some oxalic acid. In the process according to the invention the oxalic acid is coextracted with the citric acid, but is not stripped from the extract and does not contaminate the citric acid. On the other hand the accumulation of oxalic acid in the organic extractant is undesirable.

In order to lower the oxalic-acid content of the extractant the latter, after being stripped of the citric acid, is contacted with water at 120°-160°C and under pressure. A part of the oxalic acid is thus back-extracted by the water and the extractant can be recycled without accumulation of oxalic acid. Since the amount of oxalic acid extracted from the crude broth in each extraction operation is small, it is preferred that the removal of oxalic acid from the extractant be done only after at least two cycles of extraction and stripping operations.

15 Example 16

100 g of a 2% w/w aqueous solution of oxalic acid was extracted in a separatory funnel with 35 g of an extractant containing 25% w/w dilaurylbenzylamine, 69% w/w of n-octane and 6% w/w of n-octanol. After shaking at 40°C and phase separation, the aqueous raffinate was substantially free of oxalic acid. The extract contained 5.4% w/w of oxalic acid.

The extract was separated, diluted with a further 50 g of n-octane and heated to 80°C, and back-extracted with 30 g water heated to the same temperature. The oxalic acid was back-extracted almost completely. The organic extractant phase contained less than about 0.5% w/w oxalic acid.

WHAT WE CLAIM IS:—

1. A process for the recovery of an acid from an aqueous solution, which comprises extracting the aqueous solution of the acid with a water-immiscible organic extractant comprising at least one secondary or tertiary amine in which the total number of carbon atoms per molecule is at least 20, dissolved in a water-immiscible organic non-polar or polar solvent, separating the organic extract from the residual aqueous phase and stripping at a temperature higher than the temperature at which the extraction is performed, the organic extract with water to obtain an aqueous phase containing a substantial part of the acid and an organic phase containing substantially all the amine; and separating the aqueous back-extract from the organic phase.

2. A process according to claim 1, wherein the stripping is performed at a temperature at least 20°C above the temperature at which the extraction is performed.

3. A process according to claim 2, wherein the extraction is performed at room temperature and the stripping is performed at a temperature of 80°C or higher.

4. A process according to any one of claims 1 to 3, wherein the stripping is carried out at superatmospheric pressure at a

temperature above 100°C.

5. A process according to any one of claims 1 to 4, wherein the water-immiscible, polar or non-polar organic solvent comprises an aliphatic or aromatic hydrocarbon, petroleum fractions, a hydrocarbon substituted by a nitro group or a halogen atom or an alcohol, or a mixture thereof.

6. A process according to any one of claims 1 to 5, wherein prior to the stripping, one of the following operations is performed: (a) solvent is removed from the organic extract, (b) solvent, either the same as that which forms part of the extract or different from it, is added or (c) some of the solvent which forms part of the extract is replaced by a different one.

7. A process according to any one of Claims 1 to 6, wherein the extraction is performed as a continuous multi-stage counter-current process and the stripped extract is cooled or allowed to cool, to the temperature at which the extractant is performed and recycled to the extraction.

8. A process according to claim 7, 90 wherein, prior to recycling, impurities and/or acid by-products remaining in the stripped extract are removed from it, and/or further solvent or auxiliary substances that may have been added to the extract before the stripping operation are removed from it and/or make-up solvent and/or amine are added to the stripped extract.

9. A process according to any one of claims 1 to 8, wherein a part of the extracted acid is stripped with water and the remainder is then stripped with an aqueous solution of an alkali metal (including ammonium) hydroxide or an alkali metal (including ammonium) salt, in order to recover the residual acid in the form of its corresponding alkali metal or ammonium salt.

10. A process according to any one of claims 1 to 9, wherein citric acid is recovered from a citric-acid fermentation broth.

11. A process according to claim 10, wherein oxalic acid by-product remaining in the stripped extractant is at least partially removed from the stripped extractant.

12. A process according to claim 11, wherein the stripped extractant is contacted with water under pressure at a temperature of from 120°C to 160°C at least partially to remove the oxalic acid contained therein.

13. A process according to claim 11 or 12, wherein the extract is recycled for use in the first extraction and is at least partially freed of oxalic acid by-product after at least two extraction and stripping cycles.

14. A process according to claim 1 substantially as described in any one of the

foregoing Examples.

15. An acid whenever recovered by a process as claimed in any of the preceding claims.

5 16. Citric acid whenever isolated from a fermentation broth by the process of any of claims 1 to 14.

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